

ing such unused hydrogen peroxide with the carbonate is also wasted. Put in another way, the ratio of hydrogen peroxide to sodium carbonate in the percarbonate is higher than that required to achieve equally as good results. The present invention, by supplying the active oxygen separately from the carbonate permits the proper amount of active oxygen to be added with substantial savings.

The active oxygen can be supplied as ozone, hydrogen peroxide or any other peroxy compound such as calcium, magnesium, sodium or urea peroxide, alkali metal, perborate, persulphate or perphosphate and other peroxides and peracid salts.

A preferred ratio by weight of carbonate or bicarbonate to chlorine dioxide is between about 1.5 to 1 and 1.2 to 1 but this may vary considerably with good results. If the ratio is decreased much less than 1.2 to 1 the maximum concentration of chlorine dioxide which can be held in stable solution is decreased but so long as there is some carbonate or bicarbonate together with active oxygen, an increased stable concentration is achieved compared to the use of no carbonate. Saturated carbonate or bicarbonate solutions are preferred. The ratio of carbonate or bicarbonate to chlorine dioxide can be greater than 1.5 to 1.0 but little improvement results so that the increased expense is not warranted.

For optimum results, the amount of hydrogen peroxide should not be much less than 14 or 15% by weight, based on carbonate and/or bicarbonate and hydrogen peroxide, or about 0.20 part by weight per part of carbonate and/or bicarbonate. In terms of active oxygen (about 47% of hydrogen peroxide is active oxygen) this is about 0.1 part active oxygen per part of carbonate and/or bicarbonate. Thus, where active oxygen is used as such, e.g. ozone, optimum results are achieved with 0.1 part active oxygen per part of carbonate and/or bicarbonate. No noticeable improvement results by increasing the hydrogen peroxide or active oxygen beyond this amount so that the increase in cost in doing so is not warranted and the main advantage of cost saving is not achieved. As aforesaid, with the percarbonate, the amount of active oxygen comprises 0.2 part per part carbonate so that if, in the present invention, it is much more than 0.15 part per part carbonate, although there is a cost savings of 25%, it is not nearly as marked. If the amount of hydrogen peroxide or active oxygen is decreased much below this amount, i.e. 0.1 part per part carbonate and/or bicarbonate, the maximum stable  $\text{ClO}_2$  concentration achievable is decreased but so long as there is some active oxygen in the presence of the carbonate and/or bicarbonate improved results are achieved.

Where active oxygen is supplied in the form of ozone or liquid hydrogen peroxide, other basic alkali metal salts of inorganic acids containing oxygen but no chlorine in the acid radical can be used, as for example, sodium or potassium borate, sulphate, phosphate, etc. However, alkali metal carbonate and/or bicarbonate are preferred.

In preparing the chlorine dioxide solutions of the present invention, the carbonate, bicarbonate or other basic salt and the hydrogen peroxide or active oxygen are continuously fed into the water at uniform metered rates dependent on the rate of addition of chloride dioxide, which is also added at a uniform rate. In this way, the pH of the solution remains about the same over the entire period of compounding. The rate of chlorine dioxide addition depends upon the output of the  $\text{ClO}_2$  generator since a preferred form of the invention contemplates adding the  $\text{ClO}_2$  to the water as it is generated, e.g. from chlorate and acid.

In compounding the solutions of the present invention, they are maintained at a neutral or basic pH.

#### Example 3

Seventy pounds of sodium carbonate and fifteen pounds of liquid hydrogen peroxide in the form of a 35% aqueous

solution (forty five lbs. solution) were continuously added at metered rates to 90 gals. of water at room temperature over a period of 24 hours. At the same time, chlorine dioxide gas generated from sodium chlorate and sulfuric acid was bubbled continuously up into the water over the same period of twenty-four hours, after which time fifty-two pounds had been added to provide a stable chlorine dioxide concentration of 6% by weight of the total mix, which did not decrease upon standing for a period of five months.

#### Example 4

Example 3 was repeated except that sodium bicarbonate was used instead of sodium carbonate with equally good results.

Where percarbonate (70% carbonate and 30% hydrogen peroxide) is used, 100 lbs. is necessary to provide the same 70 lbs. of carbonate, which requires 30 lbs. of hydrogen peroxide, whereas in Examples 3 and 4 only 15 lbs. of hydrogen peroxide were used with equally good results. The 100 lbs. of percarbonate costs forty cents per lbs. (market price) or \$40.00 whereas 70 lbs. of sodium carbonate at \$0.04 per lb. (market price) costs \$2.80 and fifteen lbs. of liquid hydrogen peroxide at about \$0.60 per lb. (actually such peroxide is bought in the form of a 35% solution at a market price of \$0.20 per pound) costs \$9.00, the carbonate and hydrogen peroxide together costing \$11.80 compared to a cost of \$40.00 using percarbonate, almost four times more. This is indeed quite remarkable.

#### Example 5

100 lbs. of sodium percarbonate, containing 70% by weight of carbonate and 30% by weight of hydrogen peroxide, and 70 lbs. of sodium carbonate (a total of 140 lbs. of carbonate to 30 lbs. of hydrogen peroxide) were added at uniform metered rates to 180 gals. of water at room temperature over a 48 hour period while at the same time bubbling 104 lbs. of  $\text{ClO}_2$  into the water to provide a stable 6%  $\text{ClO}_2$  solution which did not decrease in concentration after standing for five months.

#### Examples 6 and 7

These examples were the same as Examples 3 and 4, except that instead of hydrogen peroxide, 7 lbs. of ozone generated between a pair of electrode plates was used with good results.

#### Example 8

Same as Example 3 except twenty lbs. of sodium peroxide was used instead of the hydrogen peroxide. The results were as good as Example 3 except that the end product contained additional sodium which is not preferred.

#### Example 9

Same as Example 3 except seventy lbs. of sodium pyrophosphate was used instead of the carbonate with good results.

#### Example 10

Same as Example 3 except seventy lbs. of sodium borate was used instead of the carbonate with good results. However, borate is not preferred where the product is to be used with food or food handling equipment because it is more toxic than carbonate.

In all the above examples, the resulting solution contained no hydrogen peroxide or active oxygen as such. Evidently, in whatever way the peroxy or active oxygen causes the  $\text{ClO}_2$  to bond to the basic salt, it disappears in the process. The  $\text{ClO}_2$  exists as such in the solution because it can be removed from the solution as  $\text{ClO}_2$  and not  $\text{Cl}_2$  and oxygen.

Also, in all the examples, the solution was neutral or basic during and after compounding.

It is known to use percarbonate, hydrogen peroxide and perborate in chlorite solutions to suppress the formation